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(54) Abstract Title  
Acrylic monomers and polymers prepared therefrom

(57) A compound or polymer (A), for example an ethylenically unsaturated functional monomer, containing at least one activated  $\text{-CH-}$  group bonded to at least two electron-withdrawing groups, is reacted with a compound (B) of the formula:  $\text{R}-\text{CH}=\text{CH}-\text{Q}$  where R represents H, an optionally substituted alkyl group or a carboxylic ester or amide group and Q is an electron-withdrawing group which is or which contains a reactive functional group or R and Q are joined to form a cyclic functional group, under alkaline conditions so that Michael addition occurs between the ethylenically unsaturated double bond of the compound (B) and the activated  $\text{-CH-}$  group of the compound (A).

A malonate polyester is reacted with a compound of the formula  $\text{CH}_2=\text{CH}-\text{Q}^1$  where  $\text{Q}^1$  is an electron-withdrawing group, to form a polyester having increased resistance to hydrolysis.

Some functional monomers are also claimed per se.

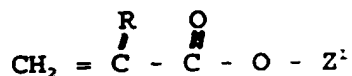
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Monomers, and Curable Compounds and Polymers

This invention relates to curable compounds and polymers having reactive functional groups useful for example in crosslinking curing reactions, to the production  
 5 of such curable compounds and polymers, to polymerisable ethylenically unsaturated monomers containing reactive functional groups and their production, and to the polymerisation of such monomers. The polymers and curable compounds can for example be used in coatings, adhesives and  
 10 sealants which cure by a crosslinking reaction.

Acrylic polymers containing reactive functional groups are well known. Such polymers can for example be prepared by addition ~~polymerisation~~ of ethylenically unsaturated monomers of the formula:-

15



where R is H or CH<sub>3</sub> and Z<sup>1</sup> for example represents an alkyl group having 1 to 4 carbon atoms substituted by a reactive functional group. We have found that such polymers often  
 20 have reduced reactivity compared to other polymers containing the same functional group. For example, an acrylic polymer containing epoxide groups derived from polymerisation of glycidyl acrylate or methacrylate has been found to be rather unreactive with amines at ambient  
 25 temperature, unlike other epoxide-functional polymers. Similar problems may be encountered with polymers of other ethylenically unsaturated monomers such as vinyl oxazolines and vinyl azlactones. Acrylic polymers, however, have advantages in coating compositions, especially the  
 30 weathering resistance and excellent gloss and clarity imparted to the coatings by acrylic polymers. There is a need for addition polymerisable ethylenically unsaturated monomers having reactive functional groups which polymerise to polymers showing better reactivity.

There is also a need for new methods of introducing reactive groups into compounds and polymers, including oligomers, which are to be used in coatings, adhesives or sealants which cure by a crosslinking reaction.

5        EP-A-634425 describes reacting a monomer/polymer having an acetoacetate group with a compound having a primary amino group in order to produce a functionalised monomer/polymer wherein the additional functional group is attached to the monomer/polymer via an enamine formed by the acetoacetate  
10 and amine groups.

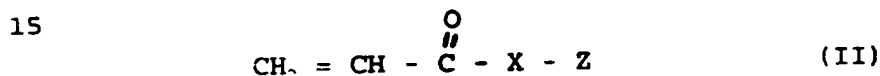
EP-A-449488 discloses azlactone-functional Michael adducts which are the Michael reaction products of 2-alkenyl azlactones and Michael donors selected from carbon and  
15 nitrogen nucleophiles. Reaction products which contain a plurality of azlactone groups are useful as step growth monomers in adhesives, sealants and coatings.

EP-A-326723 discloses a method for reacting (a) a methylene-containing component and (b) an alkene-containing component comprising mixing a tertiary amine, an epoxide,  
20 and optionally a phenolic-containing component in the presence of (a) and (b).

According to one aspect of the present invention, a process for the preparation of a polymerisable ethylenically unsaturated functional monomer is characterised in that a  
25 compound (A) containing a polymerisable ethylenically unsaturated moiety and an activated -CH- group bonded to at least two electron-withdrawing groups is reacted with a compound (B) of the formula:  $R - \overset{|}{CH} = CH - Q$  (I) where R represents H, an optionally substituted (e.g. by amide or  
30 carboxylic ester groups) alkyl group, preferably of 1 to 4 carbon atoms, or a carboxylic ester or amide group and Q is an electron-withdrawing group which is or which contains a reactive functional group or where R and Q are joined to form a cyclic functional group, under alkaline conditions so

that Michael addition occurs between the ethylenically unsaturated double bond of the compound (B) and the activated  $\overset{|}{\text{CH}}$ - group of the compound (A). By an activated  $\overset{|}{\text{CH}}$ - group we mean an activated methylene group or an activated methine group in which an H atom of an activated methylene group is replaced by a substituent which may be substantially inert, for example an alkyl group, or may be electron-withdrawing.

According to another aspect of the invention, a process for the preparation of a curable compound or polymer is characterised in that a compound or polymer (A) containing at least one activated  $\overset{|}{\text{CH}}$ - group bonded to at least two electron-withdrawing groups is reacted with an acrylate compound (B) of the formula:



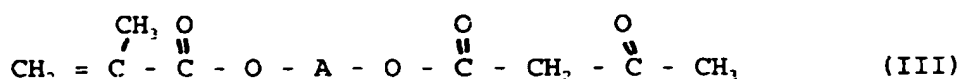
in which X represents -O- or -NH- and Z represents an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, under alkaline conditions so that Michael addition occurs between the acrylate double bond of the compound (B) and the activated  $\overset{|}{\text{CH}}$ - group of the compound or polymer (A) to produce a compound or polymer containing at least two groups Z.

According to a further aspect of the invention a process for the preparation of a curable polymer is characterised in that a polymer (A) containing at least one activated  $\overset{|}{\text{CH}}$ -group bonded to at least two electron-withdrawing groups is reacted with a compound (B) of the formula:  $\text{R} - \text{CH} = \text{CH} - \text{Q}$  where the groups R and Q are defined as above, under alkaline conditions so that Michael addition occurs between the ethylenically unsaturated double bond of the compound (B) and the activated  $\overset{|}{\text{CH}}$ - group of the polymer (A).

The activated  $\overset{|}{\text{CH}}$ - group can for example be a methylene

or methine group activated by neighbouring groups selected from carboxylic ester groups -COO-, carbonyl groups -CO-, amide groups -CONH- in which the amide nitrogen can optionally be substituted, sulphonyl groups -SO<sub>2</sub>- including  
 5 sulphonate ester and sulphonamide groups, phosphonyl groups -PO<sub>2</sub>- including phosphonate ester and phosphonamide groups or nitrile groups -CN. Examples of preferred activated -CH- groups include acetoacetate ester, malonate diester, cyanoacetate ester, sulphonoacetate ester and  
 10 phosphonoacetate ester groups. The neighbouring electron-withdrawing group is generally bonded direct to the activated -CH- group but may be a vinylogous group bonded through a -CH=CH- linkage which is conjugate with the carbonyl, nitrile, sulphonyl or phosphonyl group.

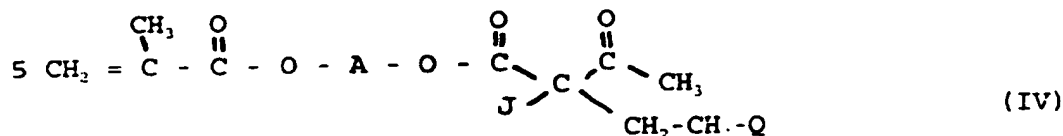
15 The unsaturated moiety present in the activated -CH- compound (A) for the preparation of the polymerisable functional monomer can for example be a methacrylate ester group or allyl group. A particularly preferred activated -CH- compound is a methacrylate ester containing  
 20 an acetoacetate, malonate or cyanoacetate group, for example acetoacetoxyalkyl methacrylate. The acetoacetoxyalkyl methacrylate preferably has the formula:-



25 in which A represents an alkylene radical having up to 10, preferably 2 to 4, carbon atoms, for example 2-acetoacetoxyethyl methacrylate (which is commercially available) or 3-acetoacetoxypropyl methacrylate.

The unsaturated compound (A) containing an activated  
 30 -CH- group can alternatively be an allyl ester such as allyl acetoacetate, allyl cyanoacetate or allyl ethyl malonate, a cyanoacetoxyalkyl methacrylate or an allyl-substituted compound such as diethyl allylmalonate.

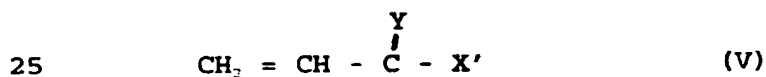
A polymerisable ethylenically unsaturated functional monomer according to yet another aspect of the invention has the formula:-



10 in which A and Q each have the meanings given above and J represents H or a group of the formula  $-\text{CH}_2 - \text{CH}_2 - \text{Q}'$ , where Q' represents a group of the formula Q, where Q has the meanings given above, or a nitrile group, a  $-\text{C}(=\text{O}) - \text{O} - \text{C}(\text{CH}_3)_2$  group or an unreactive ester group.

15 The invention also includes a polymer containing reactive functional groups which is an addition polymer comprising units of an ethylenically unsaturated functional monomer prepared by the process defined above according to the first aspect of the invention, for example a monomer of  
20 formula (IV). Such a polymer has increased reactivity compared to a polymer of the compound (I) from which monomer (IV) was prepared.

The compound (B) preferably has the formula:-



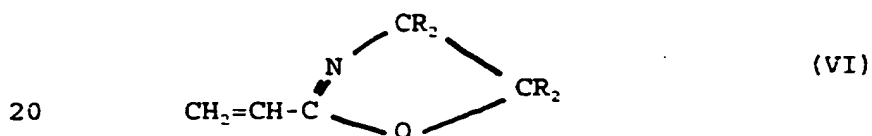
in which X' represents  $-\text{O} - \text{Z}$  or  $-\text{NR}^1\text{R}^2$  and Y represents O or a group of the formula  $=\text{N} - \text{T}$ , where Z represents an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, R<sup>1</sup> represents H or an alkyl group  
30 preferably having 1 to 6 carbon atoms and R<sup>2</sup> represents H or an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, or R<sup>1</sup> and R<sup>2</sup> together or T and Z together or T and R<sup>2</sup> together form a reactive heterocyclic ring. The reactive functional groups contained in the moiety  
35 Z can for example be epoxide, hydroxyl or isocyanate groups. The compound of formula (V) can for example be glycidyl

acrylate, 2-hydroxyethyl acrylate, N-methylol acrylamide or N-(2-hydroxyethyl) acrylamide.

The compound (B) of formula (V) can alternatively be acrylamide. After Michael addition the acrylamide group can be reacted with formaldehyde to form a methylolated acrylamide group, which can be cured at ambient temperature with a di- or poly-isocyanate or is self-crosslinking when stoved. The reaction with formaldehyde can be carried out on the monomer of formula (IV) or on the addition polymer prepared from it.

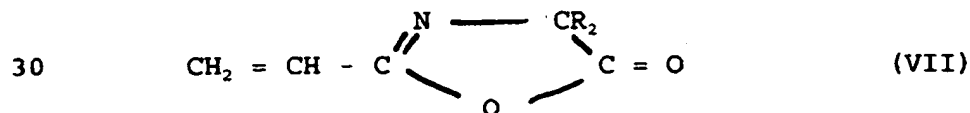
The compound (B) can alternatively be a maleate diester in which the group R of formula (I) is a carboxylic ester group.

The compound (B) can alternatively be a vinyl oxazoline of the formula:-



where each R represents H or an alkyl group, preferably of 1 to 4 carbon atoms, for example unsubstituted vinyl oxazoline. Polymers containing oxazoline groups cure for example by reaction with materials containing two or more carboxylic acid groups.

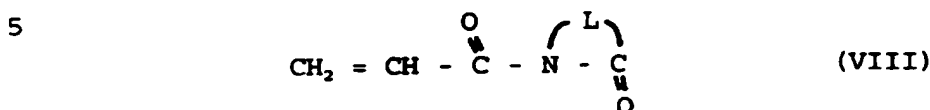
The compound (B) can alternatively be a vinyl azlactone of the formula:



where each R represents H or an alkyl group, preferably of 1 to 4 carbon atoms, for example 4,4-dimethyl-2-vinyl-azlactone. Polymers containing azlactone groups cure by

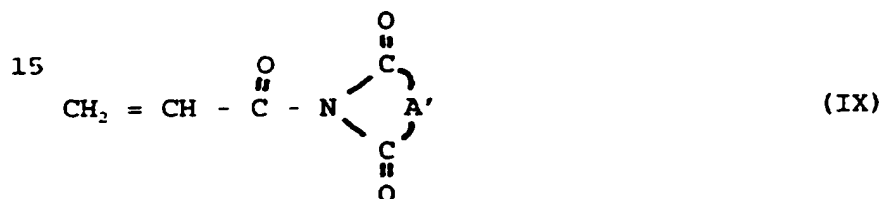
reaction with primary and secondary amino groups or thiol groups or at elevated temperature with hydroxyl groups.

The compound (B) can alternatively be an N-acryloyl lactam of the formula:-

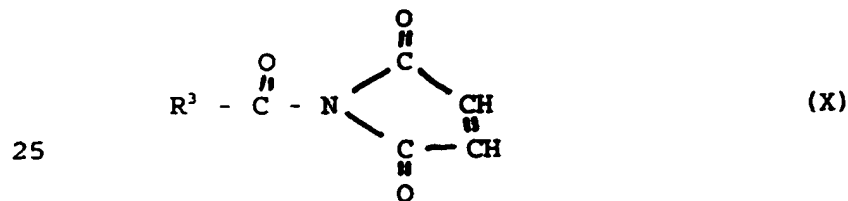


where L represents an alkylene group having 2 to 10 carbon atoms, for example N-acryloylcaprolactam. Polymers containing N-acyllactam groups cure by reaction with hydroxyl groups.

The compound (B) can alternatively be an N-acryloyl imide of the formula:-



where A' is an optionally substituted alkylene group of 2 to 4 carbon atoms or an ortho-arylene group, for example N-acryloylsuccinimide, or a maleimide of the formula:-



where R<sup>3</sup> represents an alkyl group of 1 to 18 carbon atoms. Polymers of N-acryloyl imides or N-acyl maleimides cure by reaction with compounds containing two or more hydroxyl groups.

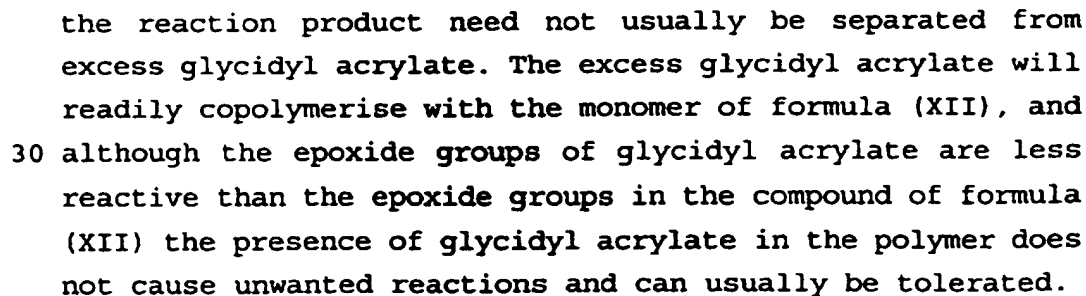
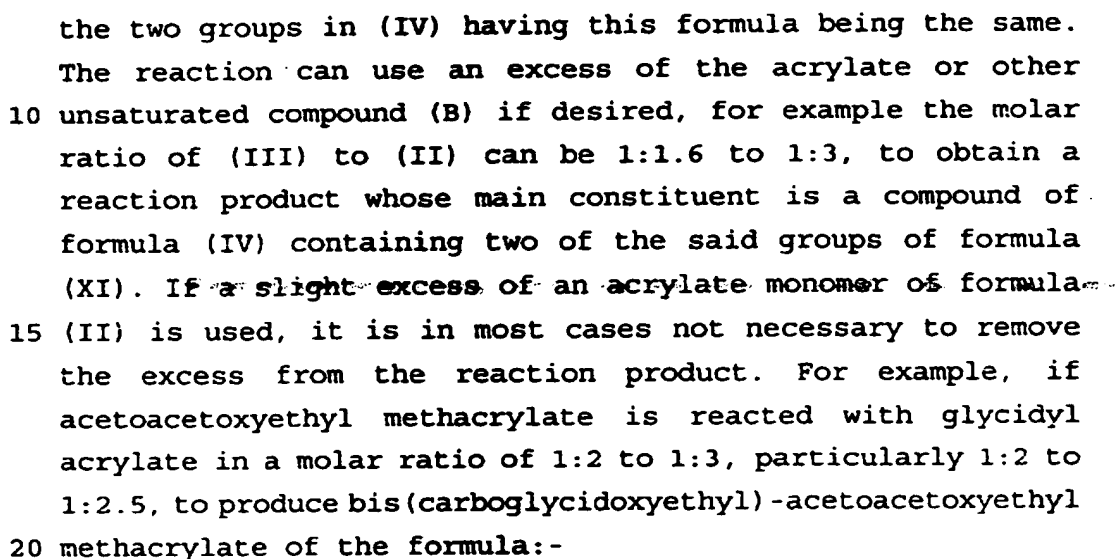
The Michael reaction between an activated  $\overset{!}{\text{CH}}$ - group and the compound (B) can in many cases be carried out in the



absence of solvent since the acetoacetate ester, cyanoacetate ester and malonate diester compounds, for example, are generally liquids (for example the acetoacetoxyalkyl methacrylates (III) are liquid) and so are  
5 most acrylate esters of formula (I). Alternatively, the reaction can be carried out in a solvent such as an aromatic hydrocarbon, an ether, a glycol ether, an ester or a ketone. The reaction is carried out under alkaline conditions, that is to say in the presence of an alkali as  
10 catalyst. The catalyst can for example be an alkoxide, for example sodium methoxide, an alkali metal hydroxide such as potassium hydroxide, potassium fluoride, a quaternary ammonium hydroxide such as tetrabutyl ammonium hydroxide or a tertiary amine such as diazabicyclooctane or  
15 ~~diazabicycloundec-7-ene~~. The reaction can be carried out at ambient temperature but is preferably carried out at elevated temperature, for example at a temperature in the range 40 to 100°C, preferably 40 to 70°C. The time of reaction is preferably in the range 10 minutes to 2 hours,  
20 for example about 1 hour at 50°C.

In Michael reactions a compound having an active hydrogen atom attached to carbon, for example a carbonyl compound existing partly in the enol form, adds across an  
25 unsaturated ester, for example an acrylate or methacrylate. We have found that methacrylate and allyl groups are much less susceptible to Michael reaction than are acrylate groups. In particular, we have found that in Michael reactions according to the invention the active methylene  
30 group of the acetoacetoxyalkyl methacrylate (III) reacts with the double bond of compound (I), for example the acrylate bond of glycidyl acrylate, with no substantial reaction with the methacrylate group present in the acetoacetoxyalkyl methacrylate.

35 The active methylene group of the acetoacetoxyalkyl methacrylate (III) has two Michael-active hydrogens and is



We have found that the two active hydrogen atoms of the 35 methylene group in acetoacetoxyethyl methacrylate have

different reactivity so that, if the acetoacetoxyalkyl methacrylate (III) and the acrylate compound (IV) are reacted in the molar proportion of about 1:1, the product consists substantially of the compound of formula (IV) in 5 which J=H. This compound can be used itself as a monomer which will introduce reactive functional groups into an acrylic polymer, or it can be further reacted with another compound having an activated double bond, for example a different compound of formula (I) introducing a different 10 functional group or an unsaturated compound conferring other properties on a polymer formed from the monomer of formula (IV). The second unsaturated compound can for example have the formula  $\text{CH}_2=\text{CH}-\text{J}$ , where J is defined as above. For example, if the compound of formula (II) which is initially 15 reacted with the acetoacetoxyalkyl methacrylate is a compound such as glycidyl acrylate introducing an epoxide functional group, the second unsaturated compound can for example be:-

- 20 (a) an acrylamide, acrylonitrile, hydroxyethyl acrylate, or tertiary amine (for example diethylaminoethyl acrylate) monomer, which may increase the reactivity of the adjacent epoxide group or provide a polar environment for epoxide reactions;
- 25 (b) tertiary butyl acrylate, which can lose the tertiary butyl group on heating and thus acts as a latent acid which will react with epoxide to provide a self-curing stoving coating system;
- 30 (c) a methylolamide such as N-methylolacrylamide, which will on heating condense with hydroxyls generated on reaction of epoxide and thus provide further cross-linking to harden a curable coating or adhesive; or
- (d) an acrylate ester not containing functional groups.

The monomers of formula (IV) and others produced by the process of the invention as defined above can be homopolymerised or copolymerised under conditions known for the production of acrylic polymers. The monomer can be used  
5 in the form in which it is prepared, either as a bulk liquid or in solution. The monomers as prepared from commercially available starting materials such as acetoacetoxyethyl methacrylate and glycidyl acrylate are stable for at least six weeks and generally for at least six months. We believe  
10 that such commercially sold methacrylates and acrylates contain inhibitors to prevent premature polymerisation, and these inhibitors also prevent premature polymerisation of the monomers produced by the process of the invention, e.g. those of formula (IV). It may be desired to wash out the  
15 residue of the alkaline catalyst before polymerisation; if so, washing is preferably carried out after storage rather than before, in case the polymerisation inhibitor is removed with the alkaline catalyst. Alternatively, it may be preferred to add polymerisation inhibitor after washing out  
20 of catalyst if it is necessary to store the monomer after washing.

Polymerisation can for example be carried out in bulk, because the monomers are generally liquid, or in organic solvent solution, aqueous emulsion or non-aqueous  
25 dispersion. Polymerisation is generally initiated by a free radical initiator, for example a peroxide such as benzoyl peroxide, an azo compound such as azobisisobutyronitrile or a redox initiator system for emulsion polymerisation. The temperature of polymerisation is generally in the range 30  
30 to 150°C and preferably 50 to 120°C. Examples of monomers which can be copolymerised with a monomer produced by the process of the invention, for example a monomer of formula (IV), are acrylic esters such as n-butyl acrylate or methacrylate, methyl methacrylate or acrylate, ethyl  
35 acrylate or methacrylate, propyl acrylate or methacrylate, n-hexyl acrylate or methacrylate, isopropyl acrylate or methacrylate, isobutyl methacrylate or acrylate, t-butyl

acrylate or methacrylate, 2-ethyl-hexyl methacrylate or acrylate, cyclohexyl acrylate or methacrylate, 2,2,5-trimethylcyclohexyl acrylate or methacrylate, isobornyl acrylate or methacrylate, acrylonitrile, methacrylonitrile 5 and vinyl compounds such as styrene, vinyl acetate or vinyl chloride.

The polymers thus produced can be used in curable coating compositions, adhesive compositions or sealant compositions together with curing agents known for curing 10 the reactive functional group present in the moiety Q of the monomer. For example, if the polymer contains units of an epoxide-functional monomer such as the monomer of formula (XII), it can be used in an ambient-temperature curing system ~~with a curing agent containing primary or secondary~~ 15 amine groups or in a heat-curable system with a curing agent containing amine, carboxylic acid or anhydride groups.

The Michael reaction between a polymer containing activated  $\text{-CH-}$  groups and the compound of formula (I) can in general be carried out under the same reaction conditions as 20 those described above for the Michael reaction of an acetoacetoxyalkyl methacrylate (III) and a compound of formula (I). The polymer can for example be an addition polymer of acetoacetoxyethyl methacrylate or a malonate polyester, for example a polyester with a glycol such as 25 ethylene glycol or neopentyl glycol (2,2-dimethylpropane-1,3-diol). The reaction can be carried out in the absence of solvent, if both the polymer and the compound of formula (I) are liquid, or it can be carried out in an organic solvent or mixture of solvents which dissolves both the polymer and 30 the compound of formula (I).

When a polymer is reacted with the compound of formula (I), the presence of unreacted (I) in the reaction product is generally undesirable. The polymer is preferably reacted with (I) in a molar ratio of 1 to 2 moles of (I) per mole of 35 activated  $\text{-CH-}$  group present in the polymer or oligomer.

Alternatively or additionally, unreacted (I) may be removed when the Michael reaction is complete.

When a compound or polymer (A) is reacted with a compound (B) of formula (II), the curable compound or polymer produced should have at least two groups Z. Most preferably, the compound (A) contains, at least two, preferably at least three, activated -CH- groups, for example acetoacetates, cyanoacetates or sulphonoacetates of polyols such as trimethylolpropane or pentaerythritol. 10 Esters of benzenesulphonoacetate acid are usually solid and may be useful in preparing solid reagents for use in powder coatings. A bis(sulphonoacetate) useful as compound (A) can be produced by reaction of a compound having two ethylenically unsaturated groups with a mercaptoacetate ester followed by oxidation of the sulphide linkage formed, 15 for example a bis(sulphonoacetate) of the formula  $\text{CH}_3\text{OOCCH}_2\text{SO}_2(\text{CH}_2)_6\text{SO}_2\text{CH}_2\text{COOCH}_3$  can be formed by reaction of 1,5-hexadiene and methyl mercaptoacetate followed by oxidation.

20 The compound or polymer (A) may contain only one activated methylene group, for example an acetoacetate, malonate, cyanoacetate or sulphonoacetate moiety. In this case, the molar ratio of compound (B) to compound or polymer (A) is at least 2:1 to ensure that the curable compound 25 produced contains two groups:

$\begin{array}{c} \text{O} \\ \parallel \\ - \text{C} - \end{array} \text{X} - \text{Z}$  derived from compound (B). If the curable compound or polymer produced according to the invention contains only two functional groups, it is preferably used 30 with a curing agent containing more than two reactive functional groups. The reaction products of sulphonoacetates such as  $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{COOCH}_3$  can be useful in producing solid difunctional reagents useful in powder coatings.

The process of the invention when applied to a polymer, 35 for example a malonate polyester, has the advantage that it

reacts out  $-\text{CH}_2-$  groups adjacent to the carboxyl of ester linkages, thereby forming a polyester of increased hydrolysis resistance. Such hydrolysis-resistant polyesters having no hydrogen atoms on the carbon adjacent to the carboxyl group are difficult to form directly, since the corresponding carboxylic acids are relatively unreactive. Thus, according to another aspect of the invention, a process for the preparation of a polyester having increased resistance to hydrolysis is characterised in that a malonate polyester is reacted with a compound (B) of the formula:  $\text{CH}_2 = \text{CH}-\text{Q}^1$ , where  $\text{Q}^1$  is a nitrile group or a group of the formula:



where  $\text{X}^2$  represents  $-\text{O}-\text{Z}^1$  or  $-\text{NR}^3\text{R}^4$  and Y represents O or a group of the formula  $=\text{N}-\text{T}^1$ , wherein  $\text{Z}^1$  represents an optionally substituted alkyl group having 1 to 6 carbon atoms and  $\text{R}^3$  and  $\text{R}^4$  each represent H or an optionally substituted alkyl group having 1 to 6 carbon atoms, or  $\text{R}^3$  and  $\text{R}^4$  together or  $\text{T}^1$  and  $\text{Z}^1$  together or  $\text{T}^1$  and  $\text{R}^4$  together form a heterocyclic ring, under alkaline conditions so that Michael addition occurs between the ethylenically unsaturated double bond of the compound (B) and the activated methylene group of the malonate moiety.

Acetoacetate, malonate or sulphonacetate groups can be incorporated into polymers with a high glass-transition temperature ( $T_g > \text{about } 30^\circ\text{C}$ ), into polymers which are crystalline solids, or into low molecular weight crystalline solids, so as to give, on Michael reaction with a compound of the formula (II), materials which still show high  $T_g$  or crystallinity useful in powder coatings. Examples of polymers with a high glass-transition temperature are polyesters based predominantly on isophthalic acid or terephthalic acid. Crystalline polyesters are frequently based on terephthalic acid, although polyurethanes are also

useful. The Michael reaction can be carried out in the melt or in solution.

The invention is illustrated by the following Examples:-

5

Example 1

Acetoacetoxyethyl methacrylate (0.1 mole, 21.4g), glycidyl acrylate (0.2 mole, 25.6g) and a molar solution of sodium in methanol (0.001 mole, 1 ml) were warmed together at about 50°C until a vigorous reaction ensued. The mixture 10 was maintained at 50°C for a further hour.

~~The product was analysed by nuclear magnetic resonance~~ (NMR) spectroscopy. <sup>13</sup>C NMR showed a predominant quaternary carbon at 61 ppm.

<sup>1</sup>H NMR showed complete removal of acrylate C=C 15 absorptions whereas the methacrylate signals were unchanged at 5.7, 6.23δ. This indicated that the product was substantially pure bis(carboglycidoxyethyl)acetoacetoxyethyl methacrylate (BGAMA).

The product was used as prepared.

20 Glycidyl-functional Copolymers

A monomer mixture of 80.7g butyl acrylate and 19.3g BGAMA with azobisisobutyronitrile (AZDN, 1g) was run into refluxing isopropanol (100g) over 2 hours and refluxed for 1 hour after the addition was complete. A second portion of 25 AZDN (0.1g) was added and reflux was continued for a further 1 hour. Volatiles were then removed under rotary evaporation. A glycidyl-functional polymer was produced at 92.5% conversion with M<sub>n</sub> (GPC, relative to polystyrene) 2750 and M<sub>w</sub> (GPC, relative to polystyrene) 6160.



Coating Composition

An amine solution was prepared from bis (methylaminocyclohexyl) methane (2g), 'DMP 30' (a tertiary amine-functional phenol) (2g), and methoxypropanol (14g).  
5 Bis(methylaminocyclohexyl) methane and 'DMP 30' are proprietary amines sold as curing agents for epoxide-functional resins.

The glycidyl-functional polymer prepared as described above (6.1g) was mixed with the amine solution (3g).

10 The mixture was cast on a glass strip with a 250 $\mu$  casting block and placed on a "Sheen" scratch recorder. Gel time was noted as the time when a permanent groove was left in the film. ~~Touch-dry time was taken as the time when the~~ groove developed ragged edges.

15 In a comparative Example, 88.34g butyl acrylate and 11.66g glycidyl methacrylate (GMA) were copolymerised under the above reaction conditions producing a glycidyl-functional polymer of  $M_n$  3870 and  $M_w$  8640 at 96.2% conversion. This polymer was used to replace the BGAMA  
20 copolymer in a coating composition having otherwise the same formulation. The results obtained are listed below:-

Time (h)	BGAMA Copolymer	GMA Copolymer
<7	liquid	liquid
35	gelled	liquid
50	film touch-dry	liquid
5 72	film touch-dry	gelled
105	film touch-dry	gelled
172	film touch-dry	gelled

It can be seen that the BGAMA copolymer cured 2 or 3 times as fast as the GMA copolymer.

- 10 The curing time to a touch-dry film of both polymers is more than that of a diglycidyl ether of bisphenol A epoxy resin.

#### Example 2

660g (5 moles) dimethyl malonate and 624g (6 moles) neopentyl glycol were heated over 6 hours while distilling off methanol at a temperature rising to 215°C to produce a neopentyl malonate polyester of Mw 2300 and Mn 615.

193g of this malonate polyester (equivalent to 1.0 mole malonate) was mixed with 256g (2 moles) glycidyl acrylate, and 20 ml 1M sodium methoxide in methanol was added over 2 hours, with 3 hours' further reaction. An epoxide-functional polymer of Mw 6800, Mn 840 and equivalent weight 224 was produced.

5g of the epoxide-functional polymer was mixed with 0.33g ethylene diamine and cast as a film. After 7 days at room temperature the film was hard and resisted 50 double rubs with methyl ethyl ketone (MEK).

2.2g epoxide-functional polymer was mixed with 1.6g trimethylolpropane tris(mercaptopropionate) and 0.04g

dimethylcocoamine and coated on an aluminium panel. After 7 days at room temperature a clear glossy film was produced which resisted 80 MEK double rubs. The film also resisted 48 hours' soaking in water with only slight blushing and 5 softening.

### Example 3

26.9g 4,4-dimethyl 2-vinyl azlactone was added to 19.8g of the neopentyl malonate polyester of Example 2 and 2.4 ml 1M sodium methoxide in methanol. The reaction mixture was 10 heated for 2 hours at 90°C to produce a viscous azlactone-functional polymer of Mw 2400 and Mn 1400.

0.3g of ~~the azlactone-functional polymer~~ and 0.007g p-toluene sulphonic acid catalyst were mixed with 2.8g hydroxy-functional polyester of equivalent weight 1400 at 15 130°C. The mixture was coated on an aluminium panel and cured at 200°C for 15 minutes to a tough flexible film.

### Example 4

47.3g acrylamide was added to 165.3g of the neopentyl malonate polyester of Example 2, followed by 20 ml 1M sodium 20 methoxide in methanol. 170.7g butyl acrylate was added over 1 hour. During addition the temperature rose to 128°C, and after addition the reaction mixture was heated at 130°C for 90 minutes to ensure that the Michael addition was complete. An opalescent syrup was produced which was an amide- 25 functional polyester in which one-third of the active hydrogen atoms of the malonate groups were replaced by -CH<sub>2</sub>CH<sub>2</sub>-CONH<sub>2</sub> groups and two-thirds by -CH<sub>2</sub>CH<sub>2</sub>-COOC<sub>4</sub>H<sub>9</sub> groups.

25.0g paraformaldehyde was added and heated at 70°C over 4 hours to produce a hydroxy-functional polymer 30 containing N-methylol amide groups, -CH<sub>2</sub>CH<sub>2</sub>CONHCH<sub>2</sub>OH and -CH<sub>2</sub>CH<sub>2</sub>CON(CH<sub>2</sub>OH)<sub>2</sub>.

6.37g of the resulting hydroxy-functional polymer was mixed with 3.40g "Desmodur N75" polyisocyanate and 0.01g dibutyltin dilaurate catalyst. The composition was coated on aluminium panels and solidified in 6 minutes to a tough 5 rubbery coating. The coating was slightly softened, but not removed, by 80 MEK double rubs.

### Example 5

67g trimethylolpropane and 237g t-butyl acetoacetate were heated together while distilling off t-butanol at 100 to 155°C. 107g t-butanol was collected, leaving a liquid oligomer comprising 1,1,1-tris(acetoacetoxymethyl)propane.

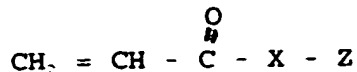
9.7g of the oligomer was gently warmed with 19.2g glycidyl acrylate and 1.5 ml 1M sodium methoxide in methanol. An exothermic Michael reaction took place, forming 15 a viscous liquid. The reaction mixture was diluted with 20g acetone and 0.1g p-toluenesulphonic acid and reacted for an hour, then stirred for a further hour with 2g calcium oxide and decolourising charcoal. After filtering and stripping, a viscous product of molecular weight about 1200 was 20 obtained which was shown by <sup>13</sup>NMR to be



8g of this hexaglycidyl oligomer epoxy resin was mixed with 1.6g trimethylhexanediamine and coated on an aluminium 25 panel. The coating set after 1 hour and cured hard overnight.

Claims

1. A process for the preparation of a curable compound or polymer, characterised in that a compound or polymer (A) containing at least one activated -CH- group bonded to at least two electron-withdrawing groups is reacted with an acrylate compound (B) of the formula:-



in which X represents -O- or -NH- and Z represents an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, under alkaline conditions so that Michael addition occurs between the acrylate double bond of the compound (B) and the activated -CH- group of the compound (A) to produce a compound or polymer containing at least two groups Z.

2. A process according to claim 1, characterised in that the compound or polymer (A) contains at least two acetoacetate ester, malonate diester, cyanoacetate ester or sulphonoacetate ester moieties in its molecule.

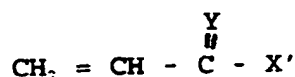
3. A process according to claim 1 or claim 2, characterised in that the compound or polymer (A) is reacted with the acrylate (B) in a molar ratio of at least about two moles of acrylate (B) per mole of activated -CH- group present in (A).

4. A process for the preparation of a polymerisable ethylenically unsaturated functional monomer, characterised in that a compound (A) containing a polymerisable ethylenically unsaturated moiety and an activated -CH- group bonded to at least two electron-withdrawing groups is reacted with a compound (B) of the formula:

$\text{R} - \text{CH} = \text{CH} - \text{Q}$  where R represents H, an optionally substituted alkyl group or a carboxylic ester or amide group and Q is an electron-withdrawing group which is or which

contains a reactive functional group or R and Q are joined to form a cyclic functional group, under alkaline conditions so that Michael addition occurs between the ethylenically unsaturated double bond of the compound (B) and the activated -CH- group of the compound (A).

5. A process according to claim 4, characterised in that the compound (B) has the formula:

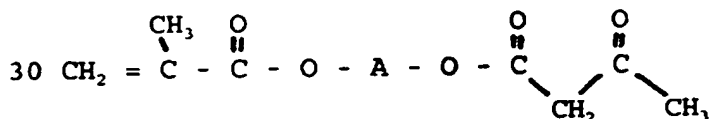


10 where X' represents -O-Z or -NR<sup>1</sup>R<sup>2</sup>, and Y represents O or a group of the formula =N-T, wherein Z represents an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, R<sup>1</sup> represents H or an alkyl group having 1 to 6 carbon atoms and R<sup>2</sup> represents H or an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, or R<sup>1</sup> and R<sup>2</sup> together or T and Z together or T and R<sup>2</sup> together form a reactive heterocyclic ring, under alkaline conditions so that Michael addition occurs between the ethylenically unsaturated double bond of the compound (B) and the activated -CH- group of the compound (A).

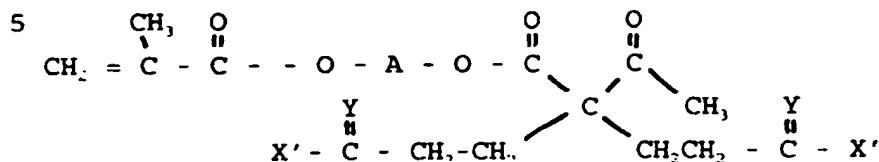
6. A process according to claim 4 or claim 5, characterised in that the unsaturated monomer (A) is a methacrylate ester containing an acetoacetate, malonate or cyanoacetate group.

25 7. A process according to claim 6, characterised in that monomer (A) is an acetoacetoxyalkyl methacrylate.

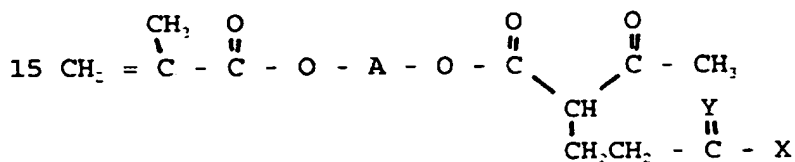
8. A process according to claim 7, characterised in that an acetoacetoxyalkyl methacrylate (A) of the formula:-



in which A represents an alkylene radical having 2 to 10 carbon atoms, is reacted with the compound (B) in a molar ratio of about 1:2 to form a polymerisable functional monomer of the formula:-

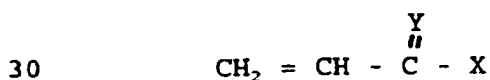


9. A process according to claim 7, characterised in  
10 that an acetoacetoxyalkyl methacrylate (A) of the formula  
(III) defined in claim 8 is reacted with the compound (B) in  
a molar ratio of about 1:1 to form a polymerisable  
functional monomer of the formula:



10. A process for the preparation of a curable polymer, characterised in that a polymer (A) containing at least one  
20 activated  $\text{-CH-}$  group bonded to at least two electron-withdrawing groups is reacted with a compound (B) of the formula:  $\text{R - CH = CH - Q}$ , where the groups R and Q are defined as in claim 4, under alkaline conditions so that Michael addition occurs between the ethylenically  
25 unsaturated double bond of the compound (B) and the activated  $\text{-CH-}$  group of the polymer (A).

11. A process according to claim 10, characterised in that the compound (B) has the formula:-



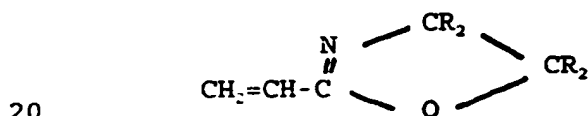
where X represents -O-Z or -NR<sup>1</sup>P<sup>2</sup>, and Y represents O or a

group of the formula =N-T, wherein Z represents an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, R<sup>1</sup> represents H or an alkyl group having 1 to 6 carbon atoms and R<sup>2</sup> represents H or an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, or R<sup>1</sup> and R<sup>2</sup> together or T and Z together or T and R<sup>2</sup> together form a reactive heterocyclic ring.

12. A process according to claim 10 or claim 11, characterised in that the polymer (A) is a polyester containing malonate diester groups.

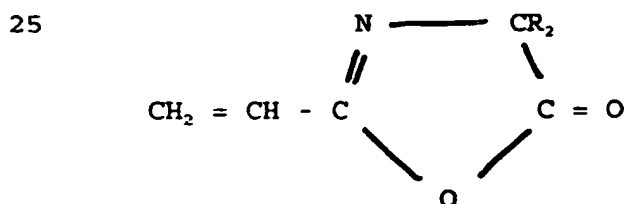
13. A process according to any of claims 1 to 12, characterised in that the compound (B) is glycidyl acrylate.

14. A process according to any of claims 4 to 12, characterised in that the compound (B) is a vinyl oxazoline of the formula:-



where each R represents H or an alkyl group.

15. A process according to any of claims 4 to 12, characterised in that the compound (B) is a vinyl azlactone of the formula:

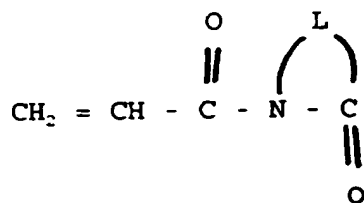


where each R represents H or an alkyl group.

30 16. A process according to any of claims 4 to 12, characterised in that the compound (B) is an N-



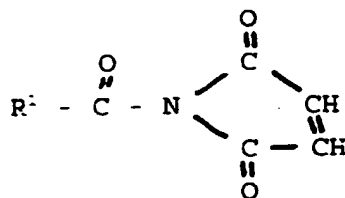
acryloyllactam of the formula:-



5 where L represents an alkylene group having 2 to 10 carbon atoms.

17. A process according to any of claims 4 to 12, characterised in that the compound (B) is an N-acyl maleimide of the formula:-

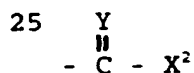
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15 where R<sup>1</sup> represents an alkyl group.

18. A process according to claim 5, characterised in that the compound (B) is acrylamide and after Michael addition the acrylamide group is reacted with formaldehyde to form a methylolated acrylamide group.

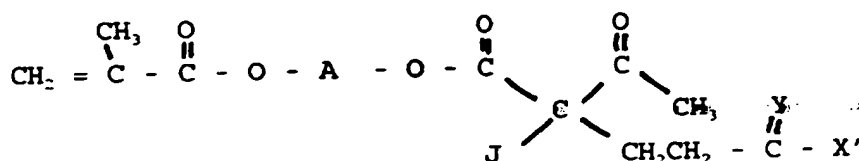
20 19. A process for the preparation of a polyester having increased resistance to hydrolysis, characterised in that a malonate polyester is reacted with a compound (B) of the formula CH<sub>2</sub>=CH-Q<sup>1</sup> where Q<sup>1</sup> is a nitrile group or a group of the formula:



where X<sup>2</sup> represents - O - Z<sup>1</sup> or -NR<sup>3</sup>R<sup>4</sup> and Y represents O or a group of the formula =N-T<sup>1</sup>, wherein Z<sup>1</sup> represents an

optionally substituted alkyl group having 1 to 6 carbon atoms and R<sup>3</sup> and R<sup>4</sup> each represent H or an optionally substituted alkyl group having 1 to 6 carbon atoms, or R<sup>3</sup> and R<sup>4</sup> together or T<sup>1</sup> and Z<sup>1</sup> together or T<sup>1</sup> and R<sup>4</sup> together form a heterocyclic ring, under alkaline conditions so that Michael addition occurs between the ethylenically unsaturated double bond of the compound (B) and the activated methylene group of the malonate moiety.

20. A polymerisable ethylenically unsaturated functional monomer of the formula:-

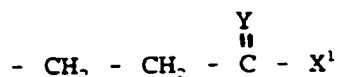


15 in which A represents an alkylene radical having 2 to 10 carbon atoms, X<sup>1</sup> represents -O-Z or -NR<sup>1</sup>R<sup>2</sup>, Y represents O or a group of the formula =N-T, wherein Z represents an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, R<sup>1</sup> represents H or an alkyl group having 1 to 6 carbon atoms and R<sup>2</sup> represents H or an alkyl group having 1 to 6 carbon atoms substituted by a reactive functional group, or R<sup>1</sup> and R<sup>2</sup> together or T and Z together or T and R<sup>2</sup> together form a reactive heterocyclic ring, and J represents H or a group of the formula -CH<sub>2</sub>CH<sub>2</sub>-Q, where Q represents a group of the formula -C(=Y)-X' where X' and Y have the meanings given above, or a nitrile group, a -C(=O)-O-C(CH<sub>3</sub>)<sub>3</sub> group or an unreactive ester group.

21. A polymerisable functional monomer according to claim 20, characterised in that Y represents O and X' represents -O-Z where Z represents an alkyl group having 1 to 4 carbon atoms substituted by a group selected from epoxide, hydroxyl and isocyanate groups.

22. A polymerisable functional monomer according to

claim 20 or claim 21, characterised in that J represents a group of the formula:-

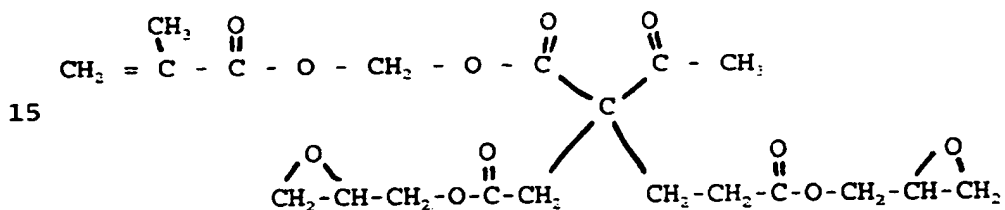


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the two groups in the compound of the formula  $-CH_2-CH_2-\overset{\overset{Y}{\parallel}}{C}-X'$  being the same.

23. A polymerisable functional monomer according to claim 21 or claim 22, characterised in that Z represents a glycidyl group.

24. Bis(carboglycidoxyethyl) acetoacetoxyethyl methacrylate of the formula:-



25. A polymer containing reactive functional groups, characterised in that the polymer is an addition polymer comprising units of a monomer prepared according to any of claims 4 to 9 or of a monomer according to any of claims 20 to 24.